

version of 6 April 1995

**Comment on symmetry of the interaction between an asymmetric rigid rotor  
and a linear rigid rotor**

Sheldon Green

NASA Goddard Space Flight Center

Institute for Space Studies

New York, NY 10025

**ABSTRACT**

In fitting an ab initio potential for  $\text{H}_2\text{O}-\text{H}_2$ , Phillips, et al. [*J. Chem. Phys.* **101**, 5824 (1994)] excluded certain terms in the angular expansion they believed to vanish because of "the requirement that the potential is invariant to inversion of all coordinates through the origin." However, there has been some question in the literature as to whether these terms must, in fact, vanish owing to spatial inversion symmetry. By providing counterexamples, it is demonstrated here that this is *not required* by fundamental spatial symmetry. However, these terms do appear to vanish for realistic molecular interactions and this symmetry may arise from the two-body nature of the electrostatic Hamiltonian.

## 1. Introduction

An accurate method for calculating energy transfer in nonreactive molecular collisions is the close coupling approach which solves the time independent Schrodinger equation by expanding the total system wavefunction in a basis set of rotation (and vibration) functions of the asymptotic molecular species and a partial wave expansion for the collision coordinate. This leads to coupled second-order differential equations for radial functions which are labeled by the asymptotic vibration-rotation states and the partial wave orbital angular momentum; the coupling comes from the orientation dependence of the interaction potential. Calculation of the required matrix elements of the interaction potential over the expansion basis functions is facilitated by expanding the orientation dependence of the potential in an appropriate complete set of orthonormal functions so that the angular part of the matrix elements can be obtained from angular momentum coupling theory.

It is always advantageous to use any symmetry inherent in the collision system to decouple the problem into smaller, noninteracting sets of states. To give the simplest example, for the case of a diatomic molecule colliding with a structureless atom<sup>1</sup> it is convenient to combine the diatomic rotational angular momentum,  $j$ , with the orbital angular momentum of the collision,  $\ell$ , to form a total angular momentum  $J$ . Because of conservation of both total angular momentum (owing to rotational invariance) and parity (owing to invariance on spatial inversion), the problem can be separated into uncoupled subsets labeled by  $J$  and by parity,  $\mathcal{P} = (-1)^{\ell+j}$ . For this case appropriate expansion functions for the interaction potential are Legendre polynomials,  $P_\lambda(\cos\theta)$ , where  $\theta$  is the angle between the diatomic bond and the collision coordinate. Molecular symmetries may limit the required angular expansion terms. For example, for homonuclear diatomic molecules only terms with even  $\lambda$  can be nonzero. Because the matrix elements for even  $P_\lambda$  terms vanish unless the rotational levels,  $j$  and  $j'$  have the same parity, one immediately obtains the collisional selection rule that  $\Delta j$  must be even, and calculations

can be done separately for the even and the odd rotational levels. Similar, if less obvious, collisional selection or "propensity" rules have been obtained for more complex systems.<sup>2</sup>

Of particular relevance to the present discussion is the symmetry of the angular terms used to describe the interaction of two linear rigid rotors.<sup>3</sup> These are labeled by three indices:  $\ell_1$  and  $\ell_2$  which describe the tensor order of the dependence on orientation of molecules 1 and 2, respectively, and  $\ell$  which is the vector sum of  $\ell_1$  and  $\ell_2$ . Because the interaction potential must be invariant to spatial inversion of the whole system and because the expansion terms with odd  $\ell_1 + \ell_2 + \ell$  change sign under this symmetry operation, these terms must vanish.

It is important that angular terms in the expansion of the interaction which must vanish owing to symmetry not be included inadvertently. This may seem like a trivial point, but it is quite possible to obtain nonzero values for such terms, e.g., when fitting a limited set of ab initio points. The problem is easily avoided if these terms are simply excluded from the fit. For most systems studied to date the appropriate symmetries have been fairly obvious. However, as computational abilities have increased, close coupling studies have been attempted for more complex collision systems where the symmetries may be less readily apparent. Recent work has focused on collisions of symmetric top ( $\text{NH}_3$ )<sup>4-7</sup> and asymmetric top ( $\text{H}_2\text{O}$ )<sup>8-10</sup> rigid rotors colliding with a linear rigid rotor,  $\text{H}_2$ , and, unfortunately, a question is raised in the literature concerning whether certain terms in the angular expansions appropriate to these systems must vanish owing to symmetry.<sup>7,11</sup> The terms in question are analogous to the odd  $\ell_1 + \ell_2 + \ell$  terms discussed above for two linear rotors. In the case of  $\text{NH}_3$  these terms affect collisional propensity rules and might explain some discrepancies between experiment and the most recent theoretical values.<sup>11</sup>

The present work addresses the question of symmetry in the interaction between an (a)symmetric rotor and a linear rotor. The next section presents the formalism and

derives some of the accepted symmetry relations. Section 3 presents numerical examples which indicate that the symmetry in question is *not* a consequence of any fundamental spatial symmetry. On the other hand it *does* appear to be generally valid for empirical functions that are expected to be typical of intermolecular forces. Also, attempts at fitting the  $\text{H}_2\text{O}-\text{H}_2$  ab initio potential in the course of work leading to Ref. 9 which did include these terms, found them to be numerically small. While the symmetry relation in question is *not* a general property of the symmetry of space to rotations, reflections, and inversion through the origin, it may, nonetheless, result from underlying symmetry of the electronic structure Hamiltonian as suggested by Rist, Valiron, and Alexander,<sup>7</sup> although the proof presented there is valid only for long-range interactions.

## 2. Coordinates and angular expansion functions

Slightly different conventions for describing the coordinates for the collision of an (a)symmetric rigid rotor with a linear rigid rotor have been used. The present work follows the convention adopted in this laboratory; the connection with other choices was discussed in Ref. 9. The overall system is described in space-fixed coordinates with origin at the collisional center of mass. The collision coordinate,  $\mathbf{R}$ , the vector from the (a)symmetric top center of mass to the linear rotor center of mass, is then conveniently described by the usual spherical polar coordinates  $(R, \Theta, \Phi)$  where  $R$  is the radial distance,  $\Theta$  is measured from the  $z$ -axis, and  $\Phi$  is measured from the  $xz$ -plane. The orientation of the linear molecule can also be described by space-fixed polar angles  $(\Theta', \Phi')$ . The orientation of the (a)symmetric top requires three angles, traditionally the Euler angles  $(\alpha, \beta, \gamma)$  which rotate the space-fixed axes to an axis system fixed in the frame of the molecule. Following earlier work we do not consider here the most general case, but assume that the top has a plane of symmetry; this is always true for symmetric tops, such as  $\text{NH}_3$ , and is also true for  $\text{H}_2\text{O}$ .<sup>9</sup> We choose the molecule-fixed axes such that the  $xz$ -plane is a plane of symmetry. If the molecule has

a two-fold or higher axis of symmetry (always true for a symmetric top) we chose this axis as the molecule-fixed z-axis; otherwise (e.g., a planar molecule such as deuterated water) we choose one of the two principal axes of inertia which are in the molecular plane (the xz-plane) as the molecule-fixed z-axis. The molecular orientation  $\alpha, \beta, \gamma = 0, 0, 0$  then corresponds to alignment of the molecule-fixed and space-fixed axis systems. A general orientation  $\alpha, \beta, \gamma$  is produced by rotating the molecule-fixed axis system, beginning at 0,0,0, by an angle  $\alpha$  about the molecule-fixed z-axis, followed by a rotation  $\beta$  about the molecule-fixed y-axis, and then another rotation  $\gamma$  about the molecule-fixed z-axis.

We choose angular expansion functions as rotationally invariant contractions of spherical harmonics for  $\Theta, \Phi$  and  $\Theta', \Phi'$  and rotation matrices for  $\alpha, \beta, \gamma$  :

$$V(R, \Theta, \Phi, \Theta', \Phi', \alpha, \beta, \gamma) = \sum_{\ell_1 m_1 \ell_2 \ell} \ell^{(R)} T_{\ell_1 m_1 \ell_2 \ell}(\Theta, \Phi, \Theta', \Phi', \alpha, \beta, \gamma) . \quad (1)$$

where

$$T_{\ell_1 m_1 \ell_2 \ell}(\Theta, \Phi, \Theta', \Phi', \alpha, \beta, \gamma) = (1 + \delta_{m_1 0})^{-1} \sum_{r_1 r_2 r} \begin{bmatrix} \ell_1 & \ell_2 & \ell \\ r_1 & r_2 & r \end{bmatrix} \quad (2)$$

$$Y_{\ell_2 r_2}(\Theta', \Phi') Y_{\ell r}(\Theta, \Phi) [D_{m_1 r_1}^{\ell_1}(\alpha, \beta, \gamma) + (-1)^{\ell_1 + m_1 + \ell_2 + \ell} D_{-m_1 r_1}^{\ell_1}(\alpha, \beta, \gamma)] .$$

Here (:::) is a Wigner 3-j symbol,  $D_{mr}^{\ell}(\alpha, \beta, \gamma)$  is a Wigner rotation matrix, and  $Y_{\ell m}(\Theta, \Phi)$  is a spherical harmonic, all as defined by Silver,<sup>12</sup> and the sum is over  $r_1$ ,  $r_2$ , and  $r$ . Eq. (1) is a generalization of the expansion terms used for two linear rotors.<sup>3</sup> Because the first molecule is no longer cylindrically symmetric it requires a rotation matrix labeled by  $\ell_1, m_1$  in place of a spherical harmonic; otherwise  $\ell_1$ ,  $\ell_2$ , and  $\ell$  serve analogous roles.

Because of rotational invariance, the intermolecular potential, and other physically meaningful quantities, can depend on only a smaller number of *relative* angles (sometimes called body-fixed angles, not to be confused with the rotor body-fixed coordinate system discussed above). In general, one can choose three angles in an

arbitrary way, corresponding to rotation of the collision system as a whole. A convenient choice does this by fixing the symmetric or asymmetric rotor orientation at  $\alpha, \beta, \gamma = 0, 0, 0$  and defining  $\theta, \varphi$  and  $\theta', \varphi'$  as the collision direction and the linear molecule orientation *relative to the rotor molecule body-fixed axis system*.<sup>9</sup> In terms of these relative coordinates Eqs. (1)-(2) can be written as

$$V(R, \theta, \varphi, \theta', \varphi') = \sum_{\ell_1 m_1 \ell_2 \ell} Y_{\ell_1 m_1 \ell_2 \ell}^{(R)} t_{\ell_1 m_1 \ell_2 \ell}(\theta, \varphi, \theta', \varphi') , \quad (3)$$

where

$$t_{\ell_1 m_1 \ell_2 \ell}(\theta, \varphi, \theta', \varphi') = (1 + \delta_{m_1 0})^{-1} \sum_{r_1 r_2 r} \begin{bmatrix} \ell_1 & \ell_2 & \ell \\ r_1 & r_2 & r \end{bmatrix} Y_{\ell_2 r_2}(\theta' \varphi') Y_{\ell r}(\theta \varphi) [\delta_{m_1 r_1} + (-1)^{\ell_1 + m_1 + \ell_2 + \ell} \delta_{-m_1 r_1}] , \quad (4)$$

$\delta_{ij}$  is a Kronecker delta, equal to one if  $i=j$  and to zero otherwise, and the sum is again over  $r_1, r_2, r$ .

Another body-fixed system has been used previously<sup>5,7,8</sup> in which the orientation of the linear molecule is measured not with respect to the water-fixed axes but with respect to the intermolecular vector,  $\mathbf{R}$ ; i.e., the body-fixed z-axis is aligned with  $\mathbf{R}$ , the body-fixed x-axis is in the plane defined by the water-fixed z-axis and  $\mathbf{R}$ , and the body-fixed y-axis is perpendicular to both  $\mathbf{R}$  and the water-fixed z-axis. The linear molecule orientation is then described by polar coordinates  $\theta'', \varphi''$  in this local, body-fixed coordinate system. Eqs. (1) and (2) are then written as

$$V(R, \theta, \varphi, \theta'', \varphi'') = \sum_{\ell_1 m_1 \ell_2 \ell} Y_{\ell_1 m_1 \ell_2 \ell}^{(R)} \tau_{\ell_1 m_1 \ell_2 \ell}(\theta, \varphi, \theta'', \varphi'') , \quad (5)$$

where

$$\tau_{\ell_1 m_1 \ell_2 \ell}(\theta, \varphi, \theta'', \varphi'') = (1 + \delta_{m_1 0})^{-1} [(2\ell + 1)/4\pi]^{1/2} \sum_{s_1} \begin{bmatrix} \ell_1 & \ell_2 & \ell \\ s_1 & -s_1 & 0 \end{bmatrix} (-1)^{s_1} Y_{\ell_2 s_1}(\theta'' \varphi'') [D_{s_1 m_1}^{\ell_1}(\varphi, \theta, 0) + (-1)^{\ell_1 + m_1 + \ell_2 + \ell} D_{s_1 -m_1}^{\ell_1}(\varphi, \theta, 0)] . \quad (6)$$

The orthonormality integrals of the expansion functions, Eqs. (2), (4), and (6), are useful for expanding the angle dependence of various quantities, such as the interaction

potential, and for calculating matrix elements.

$$\begin{aligned} & \int \sin\Theta d\Theta \, d\Phi \, \sin\Theta' d\Theta' \, d\Phi' \, d\alpha \, \sin\beta d\beta \, d\gamma \\ & T_{\ell_1 m_1 \ell_2 \ell}^{(\Theta, \Phi, \Theta', \Phi', \alpha, \beta, \gamma)*} T_{\ell'_1 m'_1 \ell'_2 \ell'}^{(\Theta, \Phi, \Theta', \Phi', \alpha, \beta, \gamma)} \\ & = 16\pi^2 (1+\delta_{m_1 0})^{-2} (2\ell_1+1)^{-1} \delta_{\ell_1 \ell'_1} \delta_{m_1 m'_1} \delta_{\ell_2 \ell'_2} \delta_{\ell \ell'} , \end{aligned} \quad (7)$$

and

$$\begin{aligned} & \int \sin\theta d\theta \, d\varphi \, \sin\theta' d\theta' \, d\varphi' \, t_{\ell_1 m_1 \ell_2 \ell}^{(\theta, \varphi, \theta', \varphi')*} t_{\ell'_1 m'_1 \ell'_2 \ell'}^{(\theta, \varphi, \theta', \varphi')} \\ & = \int \sin\theta d\theta \, d\varphi \, \sin\theta'' d\theta'' \, d\varphi'' \, \tau_{\ell_1 m_1 \ell_2 \ell}^{(\theta, \varphi, \theta'', \varphi'')*} \tau_{\ell'_1 m'_1 \ell'_2 \ell'}^{(\theta, \varphi, \theta'', \varphi'')} \\ & = 2 (1+\delta_{m_1 0})^{-2} (2\ell_1+1)^{-1} \delta_{\ell_1 \ell'_1} \delta_{m_1 m'_1} \delta_{\ell_2 \ell'_2} \delta_{\ell \ell'} . \end{aligned} \quad (8)$$

Symmetry properties of these angular functions have been discussed already in the literature, although details have not been given for the body-fixed coordinates, Eq. (4), which we prefer to use. Consider first the complex conjugate of  $t_{\ell_1 m_1 \ell_2 \ell}^{(\theta, \varphi, \theta', \varphi')}$ .

Using the relation for the complex conjugate of a spherical harmonic,

$$Y_{\ell, m}(\theta, \varphi)^* = (-)^m Y_{\ell, -m}(\theta, \varphi) , \quad (9)$$

the fact that the three projection values in a 3-j symbol must sum to zero, and the fact that

$$\begin{bmatrix} a & b & c \\ -d & -e & -f \end{bmatrix} = (-)^{a+b+c} \begin{bmatrix} a & b & c \\ d & e & f \end{bmatrix} , \quad (10)$$

it is readily shown that  $t_{\ell_1 m_1 \ell_2 \ell}^{(\theta, \varphi, \theta', \varphi')*} = t_{\ell_1 m_1 \ell_2 \ell}^{(\theta, \varphi, \theta', \varphi')}$ , i.e., that these angular expansion coefficients are real. Since the potential is real, the radial coefficients are likewise real quantities.

Consider next reflection in the rotor xz-plane, which we have taken to be a plane of symmetry. This has the effect of changing  $\varphi \rightarrow -\varphi$  and  $\varphi' \rightarrow -\varphi'$ . Using the fact that

$$Y_{\ell, m}(\theta, -\varphi) = (-)^m Y_{\ell, -m}(\theta, \varphi) , \quad (11)$$

changing signs of the projection values in the 3-j symbols using Eq. (10), which is allowed because these are dummy summation indices, and using the fact that the three

projection values sum to zero, Eq. (4) becomes

$${}^t_{\ell_1 m_1 \ell_2 \ell}(\theta, -\varphi, \theta', -\varphi') = (1 + \delta_{m_1 0})^{-1} \sum_{r_1} (-1)^{\ell_1 + \ell_2 + \ell + r_1} \begin{bmatrix} \ell_1 & \ell_2 & \ell \\ r_1 & r_2 & r \end{bmatrix} \quad (12)$$

$$Y_{\ell_2 r_2}(\theta' \varphi') Y_{\ell r}(\theta \varphi) [\delta_{m_1, -r_1} + (-1)^{\ell_1 + m_1 + \ell_2 + \ell} \delta_{-m_1, -r_1}] .$$

Because of the delta symbols,  $(-)^{r_1} = (-)^{m_1}$ . It is also obvious that  $\delta_{i,j} = \delta_{-i,-j}$ , giving finally

$${}^t_{\ell_1 m_1 \ell_2 \ell}(\theta, -\varphi, \theta', -\varphi') = {}^t_{\ell_1 m_1 \ell_2 \ell}(\theta, \varphi, \theta', \varphi') . \quad (13)$$

Thus, any function expanded as in Eq. (3) is automatically symmetric on reflection in the body-fixed xz-plane. Note that the two delta functions, which derive from the two rotation matrices in the space-fixed coordinates, Eq. (2), have been switched to accomplish this. In fact, the phased sum over  $m_1$  in Eqs. (2), (4), and (6) was chosen in the expansion functions precisely to account for reflection symmetry in the xz-plane.

As discussed in some detail by Rist, Valiron, and Alexander<sup>7</sup> the  $m_1$  index is closely related to rotation about the (a)symmetric top axis; in general, if the rotor has a  $C_{nv}$  axis of symmetry only values of  $m_1$  which are integral multiples of  $n$  are allowed. For a molecule like  $H_2O$  which has a  $C_{2v}$  axis, this is equivalent to the yz-plane as well as the xz-plane being a plane of symmetry. Rather than consider rotation about the z-axis, which was discussed by Rist, Valiron, and Alexander, we consider here reflection in the yz-plane which has the effect of taking  $\varphi \rightarrow \pi - \varphi$  and  $\varphi' \rightarrow \pi - \varphi'$ .

Using the fact that

$$Y_{\ell, m}(\theta, \pi - \varphi) = Y_{\ell, -m}(\theta, \varphi) , \quad (14)$$

changing the signs of the projection indices in the 3-j symbol, and swapping the role of the two delta functions as above, it is straightforward to show that

$${}^t_{\ell_1 m_1 \ell_2 \ell}(\theta, \pi - \varphi, \theta', \pi - \varphi') = (-1)^{m_1} {}^t_{\ell_1 m_1 \ell_2 \ell}(\theta, \varphi, \theta', \varphi') . \quad (15)$$

Because the potential must be invariant to reflection in the yz-plane,  $V(R, \theta, -\varphi, \theta', -\varphi') = V(R, \theta, \varphi, \theta', \varphi')$ , which implies that



$$\begin{aligned}
& \sum_{\ell_1 m_1 \ell_2 \ell} v_{\ell_1 m_1 \ell_2 \ell}^{(R)} t_{\ell_1 m_1 \ell_2 \ell}^{(\theta, -\varphi, \theta', -\varphi')} \\
&= \sum_{\ell_1 m_1 \ell_2 \ell} v_{\ell_1 m_1 \ell_2 \ell}^{(R)} (-)^{m_1} t_{\ell_1 m_1 \ell_2 \ell}^{(\theta, \varphi, \theta', \varphi')} \\
&= \sum_{\ell_1 m_1 \ell_2 \ell} v_{\ell_1 m_1 \ell_2 \ell}^{(R)} t_{\ell_1 m_1 \ell_2 \ell}^{(\theta, \varphi, \theta', \varphi')}
\end{aligned} \tag{16}$$

Because the expansion functions are orthonormal the equality holds separately for each angular term so that

$$(-)^{m_1} v_{\ell_1 m_1 \ell_2 \ell}^{(R)} = v_{\ell_1 m_1 \ell_2 \ell}^{(R)} , \tag{17}$$

and potential expansion coefficients with odd  $m_1$  must vanish.

We consider finally the symmetry of inverting the system through the origin, the symmetry which defines the parity of a system. Although it is agreed that this symmetry must leave the potential energy unaffected, it is the effect of this symmetry on the angular expansion functions which is somewhat controversial. Rist, Valiron, and Alexander<sup>7</sup> recently proved that terms with  $(-)^{\ell_1 + \ell_2 + \ell}$  odd must vanish owing to this symmetry for the long-range electrostatic part of the interaction. They further noted that these terms did not appear to be required in a numerical fit to the short-range part of an ab initio  $\text{NH}_3\text{-H}_2$  interaction. These terms were also found to be very small in numerical fits to an ab initio  $\text{H}_2\text{O-H}_2$  potential,<sup>9</sup> and they were excluded in the final fit.

It is easiest to consider this symmetry in the full space-fixed coordinate system of Eqs. (1) and (2). Space inversion takes a vector into its negative, i.e.,  $\mathbf{R} \rightarrow -\mathbf{R}$  which is equivalent to  $\Theta \rightarrow \pi - \Theta$ , and  $\Phi \rightarrow \Phi + \pi$ . The spherical harmonics transform as

$$Y_{\ell, m}(\pi - \Theta, \Phi + \pi) = (-)^{\ell} Y_{\ell, m}(\Theta, \Phi) . \tag{18}$$

There is no comparable transformation for the rotation matrices; in general, space inversion converts a right-handed coordinate system into a left-handed one and there is no rotation which will interconvert these. Because we have postulated a plane of

symmetry for our system, however, and because space inversion followed by reflection is equivalent to a regular rotation there is a simple transformation which describes this combination:  $\alpha \rightarrow \alpha + \pi$ ,  $\beta \rightarrow \pi - \beta$ ,  $\gamma \rightarrow \pi - \gamma$ .<sup>13</sup> The effect of this transformation on the rotation matrices is given by:

$$D_{m,r}^{\ell}(\alpha + \pi, \pi - \beta, \pi - \gamma) = e^{im(\pi - \gamma)} d_{m,r}^{\ell}(\pi - \beta) e^{ir(\alpha + \pi)} = (-1)^{\ell + m} D_{-m,r}^{\ell}(\alpha, \beta, \gamma) \quad (19)$$

where Eqs. (4.2.4) and (4.2.6) of Edmunds<sup>14</sup> have been used. Combining Eqs. (18) and (19) with Eq. (2) it is readily shown that

$$T_{\ell_1 m_1 \ell_2 \ell}(\pi - \Theta, \Phi + \pi, \pi - \Theta', \Phi' - \pi, \alpha + \pi, \pi - \beta, \pi - \gamma) = T_{\ell_1 m_1 \ell_2 \ell}(\Theta, \Phi, \Theta', \Phi', \alpha, \beta, \gamma) . \quad (20)$$

Thus, each term is separately invariant to this symmetry; it places no restrictions on the allowed terms.

It should be noted that angular terms with  $m_1 = 0$  have cylindrical symmetry about the (a)symmetric top rotor axis and thus have the same symmetry as a linear rotor; the rotation matrices in Eq. (2) reduce to a spherical harmonic for which the effect of spatial inversion can be described by Eq. (18). In this case it is straightforward to show that terms with odd  $\ell_1 + \ell_2 + \ell$  do, in fact, vanish owing the spatial inversion symmetry.

### 3. Empirical potentials

Studies of  $\text{NH}_3\text{-H}_2$ <sup>4-7</sup> and  $\text{H}_2\text{O-H}_2$ <sup>8-10</sup> to date have been based on fits to ab initio points on the interaction potential energy surface. It is important in such fits to impose the appropriate symmetries from the outset; otherwise it is easy to find spurious contributions from fits to limited numbers of points. If a particular angular term,  $X_{\lambda}(\Omega)$ , vanishes owing to some symmetry,  $\mathcal{S}$ , which transforms the angles according to  $\mathcal{S}\Omega = \Omega'$ , then it is important to include both  $\Omega$  and  $\Omega'$  in the fit (for all  $\Omega$ ) to ensure that  $X_{\lambda}$  does, in fact, go to zero in the fit. Of course, even if symmetrically related points are not specifically included, fits should converge to zero for such

symmetry forbidden terms if enough angular points are available, but this convergence can be quite slow. For an (a)symmetric top and a linear rotor, there are four angular degrees of freedom, which makes it very difficult to obtain adequate numbers of points to ensure such convergence.

On the other hand, if an interaction potential can be readily obtained (e.g., analytically) for arbitrary orientations, it is straightforward to obtain the angular expansion terms using orthogonality relationships, Eq. (8), and four-dimensional numerical quadrature. In particular, the body-fixed integrals over  $d(\cos\theta)$  and  $d(\cos\theta')$  are done with standard Gauss-Legendre quadratures and integrals over  $\varphi$  and  $\varphi'$  are done with even spaced (Gauss-Mehler) quadratures. The present work has analyzed a number of "empirical" analytic potential energy functions into angular expansion terms in the hope of shedding some light on symmetry properties. Most of the calculations were done for  $\text{H}_2\text{O}-\text{H}_2$ , but  $\text{NH}_3-\text{H}_2$  and  $\text{HDO}-\text{H}_2$  which have different symmetry were also considered. The geometries describing each of these systems are listed in Table 1; note that the molecules are placed with their center of mass at the origin, with the symmetry axis along the z-axis, and with the xz-plane a plane of symmetry, as required for the internal coordinates specified by Eq. (4). The interaction potentials were assumed to be functions only of interatomic distances, which are readily calculated from the atomic coordinates in Table 1 and the  $\text{H}_2$  coordinates. The latter are easily calculated for arbitrary collision coordinates by starting at the center of the  $\text{H}_2$  molecule which is located at polar coordinates,  $R, \theta, \varphi$ , and adding or subtracting cartesian coordinates corresponding to the polar coordinates  $R_{\text{HH}}/2, \theta', \varphi'$ , where the hydrogen bond length has been taken as  $R_{\text{HH}} = 1.4022 \text{ a}_0$  ( $1 \text{ a}_0 = \text{Bohr radius} = 5.292 \times 10^{-9} \text{ cm}$ ). Since the interaction depends only on interatomic distances *it must be invariant to all spatial symmetries*: overall rotation, reflection, or space inversion. All the empirical potentials were further designed to reflect exchange of identical particles. If the  $\text{H}_2$  hydrogens are designated as  $\text{H}_a$  and  $\text{H}_b$  and the  $\text{H}_2\text{O}$  hydrogens as  $\text{H}_1$  and  $\text{H}_2$ , atom-atom potential

terms,  $V_x(R_{1a})$ ,  $V_x(R_{2a})$ ,  $V_x(R_{1b})$ ,  $V_x(R_{2b})$ , where the notation for atom-atom distances should be evident, were always included symmetrically.

Several calculations were done using pairwise additive atom-atom interactions; this is a very common model for interaction potentials and is thought to provide a reasonably accurate description of short-range forces, which are of most concern. The atom-atom forms were either a Lennard-Jones,

$$V_{LJ}(R_m, \epsilon, R) = \epsilon [(R_m/R)^{12} - 2 (R_m/R)^6] , \quad (21)$$

or a simple exponential repulsion

$$V_{exp}(A, \alpha, R) = A \exp (-R/\alpha) . \quad (22)$$

The potential parameters were chosen rather arbitrarily and are included in Table 1.

Convergence of selected expansion terms for  $H_2O-H_2$  using the pairwise additive Lennard-Jones potential, Eq. (21), at a collision distance of  $R=4 a_0$  is shown as a function of the number of integration points (the same number was used for each of the four dimensions) in Table 2. It turns out that this interaction potential is highly anisotropic. Nonetheless these terms with relatively low indices show reasonable convergence *except for terms with  $\ell_1+\ell_2+\ell$  odd*. The latter are found to approach zero, but require relatively large numbers of integration points for convergence. Interestingly, convergence of these terms is much slower using even numbers of points. (It should, perhaps, be noted that the smallest number of integration points reported in Table 2 corresponds to two orders of magnitude more orientations than have been available in even the largest ab initio studies.) Results using a pairwise additive exponential interaction, Eq. (22), were entirely analogous and are not shown; this calculation like all the others reported here was done for a collision distance  $R=4 a_0$ .

Results for  $NH_3-H_2$  using a pairwise additive exponential function are shown in Table 3. They too are seen to be entirely analogous to results for  $H_2O-H_2$  in Table 2. Similar calculations with a pairwise additive exponential interaction for  $HDO-H_2$ , one which set the H-H and H-D interactions equal (as expected from the Born-Oppenheimer

approximation) and another which used a different interactions (H-D stronger than H-H by a factor of two) also showed the same behavior, and results are not presented here. Expansion terms which are expected to vanish owing to other symmetries in these systems, for example, terms with odd  $\ell_2$  or, for  $\text{H}_2\text{O}-\text{H}_2$ , terms with odd  $\ell_1$  or  $m_1$ , were also examined and found to converge quickly to zero; for most of these the symmetrically related points are included automatically in the integration scheme and so cancel even for very small numbers of integration points.

It appears that terms with odd  $\ell_1+\ell_2+\ell$  generally vanish for these pairwise additive atom-atom potentials, although relatively large numbers of integration points are needed to obtain numerically small values. This may be a general property of potentials which can be written as pairwise additive atom-atom interactions as suggested by Briels,<sup>15</sup> although his derivation was limited specifically to pairwise inverse powers and/or exponentials and also to collision distances large enough that atoms of the two species do not interpenetrate.

It therefore seemed reasonable to consider more general forms for the interaction potential, for example, three-body terms. As noted by Cooper and Hutson,<sup>16</sup> an important three-body term, especially at long-range, is the triple dipole interaction. A simplified functional form based on the triple dipole term was therefore considered:

$$V_{\text{ddd}} = \alpha (3 \cos\theta_1 \cos\theta_2 \cos\theta_3 + 1) r_1^{-3} r_2^{-3} r_3^{-3} \quad (23)$$

where the angles refer to the interior angles of the triangle formed by three atoms,  $r_i$  are the distances which form the sides of the triangle, and  $\alpha$  is a proportionality constant. A calculation was done for  $\text{H}_2\text{O}-\text{H}_2$  including this terms for the  $\text{H}_2$  hydrogens with each of the  $\text{H}_2\text{O}$  atoms, and using  $\alpha=3000$  for the interaction with oxygen,  $\alpha=1000$  for the interaction with the hydrogens, distances in atomic units, and numbers of integration points,  $N = 8, 15$ , and  $21$ . The odd  $\ell_1+\ell_2+\ell$  terms, however, converged smoothly to zero for this interaction in a manner analogous to that seen in Tables 2 and 3..

Although it was beginning to appear that restriction to even  $\ell_1+\ell_2+\ell$  might be a general property, some other, essentially *ad hoc* functional forms were also tried, a few of which did, in fact, provide counterexamples. These were all done for H<sub>2</sub>O-H<sub>2</sub>; to describe these it will be convenient to label the atom-atom distances as  $R_{1a}$ ,  $R_{1b}$ ,  $R_{2a}$ ,  $R_{2b}$  for distances between hydrogens in the H<sub>2</sub> (labeled a and b) and those in H<sub>2</sub>O (labeled 1 and 2) and  $R_{Oa}$  and  $R_{Ob}$  for distances between the oxygen and the two atoms in H<sub>2</sub>. The first function which was found to require odd  $\ell_1+\ell_2+\ell$  terms multiplied the pairwise additive exponential interaction discussed above by the factor:

$$\text{factor} = \exp(-R_{1a}R_{1b}/10) * \exp(-R_{2a}R_{2b}/10) , \quad (24)$$

where distances are in atomic units. Selected angular expansion terms for this interaction are shown in Table 4. Although the pattern of convergence on using more integration points was similar to that found for other interactions, it is clear that odd  $\ell_1+\ell_2+\ell$  terms do *not* vanish.

Another function for which the odd  $\ell_1+\ell_2+\ell$  terms did not vanish was obtained by multiplying the pairwise additive exponential interaction by the factor:

$$\text{factor} = 4 \times 10^{21} (R_{1a}+R_{1b}+R_{2a}+R_{2b})^{-12} (R_{Oa}+R_{Ob})^{-12} . \quad (25)$$

Expansion terms converged with respect to number of integration points are shown in Table 5. Another counterexample which does not include a pairwise additive factor is

$$V = 5 \times 10^4 \exp[-(R_{1a}+R_{1b}+R_{2a}+R_{2b})/3.5] \exp[-(R_{Oa}+R_{Ob})/2.5] . \quad (26)$$

Expansion terms for this function are also shown in Table 5. A handful of other functional forms -- of varying plausibility as representative of interaction potentials -- were tried; many could be expanded using only even  $\ell_1+\ell_2+\ell$  terms but at least one more was found which required odd terms.

#### 4. Discussion

Several simple models for the interaction potential between an (a)symmetric top rotor and a linear rotor were expanded in terms of the angular functions used in

quantum molecular scattering calculations. These angular expansion functions are labeled by indices  $\ell_1$  and  $\ell_2$ , which describe the tensor order of the dependence of the interaction on orientation of molecules 1 and 2, respectively, and  $\ell$  which is the vector sum of  $\ell_1$  and  $\ell_2$ . The chosen functions could be readily evaluated analytically for any specified collision orientation, so the angular expansion terms could be determined by converged four-dimensional numerical quadratures. There has been some controversy in the literature whether terms with odd  $\ell_1+\ell_2+\ell$  must vanish owing to spatial symmetry. For some of the functions considered here these terms were found to be nonzero. Because the potential energy functions considered here depend only on interatomic distances and because allowed spatial symmetry operations must preserve these distances, the functions considered here must be invariant to these symmetries. The fact that some functions were found which required expansion terms with odd  $\ell_1+\ell_2+\ell$  demonstrates that *such terms cannot be excluded on the grounds of the underlying symmetry of space itself*, i.e., rotations, reflections, or inversion.

On the other hand, it is possible that the electronic structure Hamiltonian has additional symmetries which exclude such terms from realistic potential energy functions. This Hamiltonian consists of two-body interactions, specifically simple inverse powers of distances, and such terms are often found to lead to only even  $\ell_1+\ell_2+\ell$  terms,<sup>7,15,17</sup> although a proof for the general case does not yet seem to be available. Because of its importance for fitting interaction potentials to use in molecular scattering calculations further work to prove the generality (or falsehood) of this conjecture would be most useful.

## ACKNOWLEDGEMENTS

This work was supported in part by NASA Headquarters, Office of Space Science and Applications, Astrophysics Division, Infrared and Radio Astrophysics Program. I am grateful to David Flower, Bruce Haas, Jeremy Hutson, Tim Phillips, Claire Rist, and

Pierre Valiron for informative discussions on this subject.



## REFERENCES

1. A. M. Arthurs and A. Dalgarno, Proc. R. Soc. A **256**, 540 (1960).
2. A small sampling of work in this area includes: M. H. Alexander, J. Chem. Phys. **77**, 1855 (1982); M. H. Alexander and D. C. Clary, Chem. Phys. Lett. **97**, 319 (1983); M. H. Alexander and P. J. Dagdigian, J. Chem. Phys. **83**, 2191 (1985); M. H. Alexander and G. C. Corey, J. Chem. Phys. **84**, 100 (1986).
3. K. Takayanagi, Adv. At. Mol. Phys. **1**, 149 (1965); S. Green, J. Chem. Phys. **67**, 715 (1977).
4. G. D. Billing and G. H. F. Diercksens, Chem. Phys. **118**, 161 (1987); **124**, 77 (1988).
5. A. Offer and D. Flower, J. Phys. B **22**, L439 (1989); A. Offer and D. Flower, J. Chem. Soc. Faraday Trans. **86**, 1659 (1990).
6. J. Schleipen, J. J. ter Meulen, and A. Offer, Chem. Phys. **171**, 347 (1993).
7. C. Rist, M. H. Alexander, and P. Valiron, J. Chem. Phys. **98**, 4662 (1993).
8. V. Balasubramanian, G. G. Balint-Kurti, and J. H. van Lenthe, J. Chem. Soc. Faraday Trans. **89**, 2239 (1993).
9. T. R. Phillips, S. Maluendes, A. D. McLean, and S. Green, J. Chem. Phys. **101**, 5924 (1994).
10. T. R. Phillips, S. Maluendes, and S. Green, J. Chem. Phys. in press (15 Apr. 1995).
11. D. R. Flower and A. Offer, in *Molecules and Grains in Space*, ed. I. Nenner, (New York, AIP Press, 1994), p. 477.
12. B. L. Silver, *Irreducible Tensor Methods: An Introduction for Chemists* (New York: Academic Press, 1975).
13. E. P. Wigner, *Group Theory*, translated by J. J. Griffin (New York: Academic Press, 1959), p. 217. Note that Wigner specifies the transformation which takes a dipod oriented at  $\alpha, \beta, \gamma$  into the dipod obtained by space inversion as  $\alpha \rightarrow \alpha \pm \pi$ ,

$\beta \rightarrow \pi\text{-}\beta$ ,  $\gamma \rightarrow \pi\text{-}\gamma$ , suggesting that this transformation may be more general than the inversion-rotation discussed here.

14. A. R. Edmunds, *Angular Momentum in Quantum Mechanics* (Princeton: Princeton University Press, 1957).
15. W. J. Briels, J. Chem. Phys. **73**, 1860 (1980); see especially the comment following Eq. (3.8).
16. A. R. Cooper and J. M. Hutson, J. Chem. Phys. **98**, 5337 (1993).
17. R. A. Sack, J. Math. Phys. **5**, 245, 253 (1964).

Table 1. Geometries and potential parameters for H<sub>2</sub>O, NH<sub>3</sub>, and HDO with H<sub>2</sub>.

H <sub>2</sub> O	coordinates (x,y,z), a <sub>0</sub>		
O	0.	0.	0.1239
H <sub>1</sub>	-1.4303	0.	-0.98323
H <sub>2</sub>	0.4303	0.	-0.98323
potential parameters, distances in a <sub>0</sub> , energies in cm <sup>-1</sup>			
H-H	R <sub>m</sub> =4.5	ε=40	A=30,000 α=3.5
O-H	R <sub>m</sub> =5.5	ε=80	A=50,000 α=2.5
NH <sub>3</sub>	coordinates (x,y,z), a <sub>0</sub>		
N	0.	0.	0.127
H <sub>1</sub>	1.7710	0.	-0.5928
H <sub>2</sub>	-0.8855	1.5337	-0.5928
H <sub>3</sub>	-0.8855	-1.5337	-0.5928
potential parameters, distances in a <sub>0</sub> , energies in cm <sup>-1</sup>			
H-H	A=3000	α=3.0	
O-H	A=4000	α=3.5	
HDO	coordinates (x,y,z), a <sub>0</sub>		
O	0.13591	0.	0.13326
H	-1.41255	0.	1.06817
D	-0.38093	0.	-1.60013
potential parameters, distances in a <sub>0</sub> , energies in cm <sup>-1</sup>			
H-H	A=10,000	α=3.5	
O-H	A=50,000	α=2.5	

---

Table 2. Convergence of selected angular expansion terms for  $\text{H}_2\text{O}-\text{H}_2$  with the Lennard-Jones interaction as a function of number of Gauss integration points. Terms with odd  $\ell_1+\ell_2+\ell$  are indicated with an asterisk. Number in parentheses is power of ten.

$\ell_1$	$m_1$	$\ell_2$	$\ell$	number of Gauss points						
				12	15	18	21	24	32	48
0	0	0	0	3.0( 6)	3.1( 6)	3.1( 6)	3.1( 6)	3.06( 6)	3.06( 6)	3.06( 6)
1	0	0	1	4.2( 6)	4.3( 6)	4.3( 6)	4.3( 6)	4.26( 6)	4.26( 6)	4.26( 6)
1	0	2	1	-2.5( 6)	-2.6( 6)	-2.6( 6)	-2.6( 6)	-2.62( 6)	-2.62( 6)	-2.62( 6)
1	0	2	3	3.9( 6)	4.0( 6)	4.0( 6)	4.0( 6)	3.95( 6)	3.95( 6)	3.95( 6)
2	2	0	2	2.3( 6)	2.3( 6)	2.3( 6)	2.3( 6)	2.35( 6)	2.35( 6)	2.35( 6)
2	2	2	0	7.9( 5)	9.0( 5)	9.0( 5)	9.0( 5)	9.00( 5)	9.01( 5)	9.01( 5)
2	2	2	1*	2.6( 4)	5.0( 0)	1.0( 3)	-4.3(-5)	2.30( 1)	8.47(-2)	4.46(-7)
2	2	2	2	-1.1( 6)	-1.2( 6)	-1.2( 6)	-1.2( 6)	-1.22( 6)	-1.22( 6)	-1.22( 6)
2	2	2	3*	-3.1( 4)	-5.1( 0)	-1.1( 3)	-1.3(-3)	-2.32( 1)	-8.03(-2)	-3.76(-7)
2	2	2	4	2.1( 6)	2.2( 6)	2.2( 6)	2.2( 6)	2.19( 6)	2.19( 6)	2.19( 6)
4	4	2	2	2.6( 5)	6.4( 5)	6.3( 5)	6.4( 5)	6.44( 5)	6.44( 5)	6.44( 5)
4	4	2	3*	1.1( 5)	1.1( 1)	5.9( 3)	6.4(-3)	1.52( 2)	6.30(-1)	3.67(-6)
4	4	2	4	-5.8( 5)	-8.1( 5)	-8.0( 5)	-8.1( 5)	-8.08( 5)	-8.09( 5)	-8.09( 5)
4	4	2	5*	-9.9( 4)	-1.0( 1)	-4.3( 3)	-3.0(-3)	-9.82( 1)	-3.66(-1)	-1.88(-6)
4	4	2	6	1.5( 6)	1.7( 6)	1.7( 6)	1.7( 6)	1.67( 6)	1.67( 6)	1.67( 6)

Table 3. Same as Table 2, but using a pairwise additive exponential interaction potential for  $\text{NH}_3\text{-H}_2$ .

$\ell_1$	$m_1$	$\ell_2$	$\ell$	number of Gauss points			
				8	11	14	20
0	0	0	0	3.155( 5)	3.155( 5)	3.155( 5)	3.155( 5)
0	0	2	2	1.303( 3)	1.303( 3)	1.303( 3)	1.303( 3)
3	0	0	3	-3.141( 3)	-3.141( 3)	-3.141( 3)	-3.141( 3)
3	0	2	1	1.403( 1)	1.389( 1)	1.389( 1)	1.389( 1)
3	0	2	3	-8.602( 1)	-8.595( 1)	-8.595( 1)	-8.595( 1)
3	3	0	3	1.890( 3)	1.890( 3)	1.890( 3)	1.890(-3)
3	3	2	1	-8.114( 0)	-8.356( 0)	-8.356( 0)	-8.356( 0)
3	3	2	2 <sup>*</sup>	-6.948(-2)	1.496(-6)	7.008(-6)	8.641(-8)
3	3	2	3	5.164( 1)	5.171( 2)	5.171( 1)	5.171( 1)
3	3	2	4 <sup>*</sup>	3.077(-2)	3.108(-5)	-3.375(-6)	-3.969(-8)
3	3	2	5	2.160( 2)	2.160( 2)	2.160( 2)	2.160( 2)

Table 4. Convergence as a function of number of Gauss integration points for selected angular expansion terms for the H<sub>2</sub>O-H<sub>2</sub> pairwise additive exponential interaction multiplied by the factor given in Eq. (24). Terms with odd  $\ell_1+\ell_2+\ell$  are indicated with an asterisk. Number in parentheses is power of ten.

$\ell_1$	$m_1$	$\ell_2$	$\ell$	number of Gauss points			
				9	12	15	24
2	2	0	2	8.3983( 2)	8.3981( 2)	8.3983( 2)	8.3983( 2)
2	2	2	0	9.3548( 1)	9.3490( 1)	9.3548( 1)	9.3548( 1)
2	2	2	1 <sup>*</sup>	-1.2276( 2)	-1.2274( 2)	-1.2276( 2)	-1.2276( 2)
2	2	2	2	1.5307( 2)	1.5310( 2)	1.5307( 2)	1.5307( 2)
2	2	2	3 <sup>*</sup>	-1.4298( 2)	-1.4300( 2)	-1.4298( 2)	-1.4298( 2)
2	2	2	4	2.7853( 2)	2.7852( 2)	2.7853( 2)	2.7853( 2)
3	2	0	3	8.3521( 2)	8.3519( 2)	8.3521( 2)	8.3521( 2)
3	2	2	1	4.1774( 1)	4.1719( 1)	4.1770( 1)	4.1770( 1)
3	2	2	2 <sup>*</sup>	-5.8239( 1)	-5.8273( 1)	-5.8239( 1)	-5.8239( 1)
3	2	2	3	1.0600( 2)	1.0605( 2)	1.0601( 2)	1.0601( 2)
3	2	2	4 <sup>*</sup>	-1.0364( 2)	-1.0363( 2)	-1.0364( 2)	-1.0364( 2)
3	2	2	5	3.2128( 2)	3.2127( 2)	3.2128( 2)	3.2128( 2)
4	4	0	4	4.6665( 1)	4.6421( 1)	4.6665( 1)	4.6665( 1)
4	4	2	2	3.4711( 0)	2.8429( 0)	3.4710( 0)	3.4710( 0)
4	4	2	3 <sup>*</sup>	-5.3440( 0)	-5.1105( 0)	-5.3449( 0)	-5.3449( 0)
4	4	2	4	1.1656( 1)	1.1791( 1)	1.1656( 1)	1.1656( 1)
4	4	2	5 <sup>*</sup>	-1.2677( 1)	-1.2758( 1)	-1.2676( 1)	-1.2676( 1)
4	4	2	6	4.0559( 1)	4.0548( 1)	4.0559( 1)	4.0559( 1)

Table 5. Angular expansion terms for the functions described by Eqs. (25) and (26) in the text. Terms with odd  $\ell_1 + \ell_2 + \ell$  are indicated with an asterisk. N is the number of Gauss points; comparison with results for smaller N indicate that these values are converged. Number in parentheses is power of ten.

$\ell_1$	$m_1$	$\ell_2$	$\ell$	Eq. (25)	Eq. (26)
				N = 27	N = 24
0	0	0	0	3.077( 2)	4.286( 2)
0	0	2	2	3.794( 1)	1.393( 1)
1	0	0	1	5.728( 2)	3.913( 2)
1	0	2	1	-4.113( 1)	-5.556( 0)
1	0	2	3	5.958( 1)	1.313( 1)
2	0	0	2	4.222( 2)	1.163( 2)
2	0	2	0	1.978( 1)	6.160(-1)
2	0	2	2	-2.646( 1)	-1.577( 0)
2	0	2	4	4.263( 1)	4.107( 0)
2	2	0	2	3.843( 1)	2.309( 1)
2	2	2	0	2.520( 0)	3.678(-1)
2	2	2	1*	-1.075( 0)	-1.970(-1)
2	2	2	2	-1.091( 0)	3.590(-2)
2	2	2	3*	-1.522( 0)	-2.607(-1)
2	2	2	4	6.092( 0)	1.687( 0)
3	0	0	3	1.879( 2)	8.512( 0)
3	0	2	1	9.500( 0)	-1.159(-1)
3	0	2	3	-1.172( 1)	-3.400(-1)
3	0	2	5	1.658( 1)	-8.264(-1)
3	2	0	3	5.157( 1)	1.677( 1)

3	2	2	1	3.055( 0)	2.033(-1)
3	2	2	2 <sup>*</sup>	-6.142(-1)	-8.099(-2)
3	2	2	3	-2.228( 0)	1.272(-2)
3	2	2	4 <sup>*</sup>	-1.548( 0)	-1.721(-1)
3	2	2	5	8.666( 0)	1.669( 0)

---